Structure and reactivity of the beta-agostic [ansa-Cp-arene]Ta(Pr-n) cation

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Supporting Information to:

Structure and reactivity of the *β*-agostic [*ansa*-Cp-arene]Ta(^{n}Pr) cation: ambivalent behaviour induced by intramolecular arene coordination

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Part I: Experimental Section

General Considerations. All manipulations were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene, hexane, and pentane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Diethyl ether and THF (Aldrich, anhydrous, 99.8%) were dried over Al_2O_3 (Fluka). Cyclohexane (Labscan) was distilled from Na/K alloy, bromobenzene (Merck) from CaH_2. All solvents were degassed prior to use and stored under nitrogen. Deuterated solvents were vacuum transferred from Na/K alloy (C_6D_6 and THF-d_8, Aldrich) or from CaH_2 (C_6D_5Br, Aldrich), and stored under nitrogen. H_2 (AGA, 99.9%) was passed over a column of $LiAlH_4$ prior to use. $TaCl_5$ (99.99%, Fluka), Me_2Zn (2.0 M in toluene, Aldrich), ^{n}PrMgCl (2.0 M in Et_2O, Aldrich), $[PhNMe_2H][B(C_6F_5)_4]$ (Strem), CO (Praxair) and PhSSPh (Fluka) were used as received. The reagent [Ar-CMe_2-C_5H_4]Li (Ar = 3,5-dimethylphenyl) was synthesized according to a published procedure.[1] NMR spectra were recorded on a Varian Inova 500 spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm); *J* is reported in Hz. Assignment of NMR resonances was aided by gradient-selected COSY, NOESY, HSQC and/or HMBC experiments using standard pulse sequences. For the ionic compounds **3**-**6**, NMR data for the $B(C_6F_5)_4$ anion are virtually identical and reported once at the end of the experimental section. IR spectra were recorded on an Interspec 301-X spectrometer inside a glovebox. Samples were prepared as films on KBr plates by evaporation of a solution of the compound, or as nujol mulls between KBr plates. Elemental analyses were performed at the Microanalytical Department of the University of Groningen or Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany).

Synthesis of [Ar-CMe_2-η^5-C_5H_4]$TaMe_3Cl$ (1). To a suspension of $TaCl_5$ (1.8 g, 5.0 mmol) in 30 mL of toluene was added $ZnMe_2$ (4.2 mL of a 2.0 M solution in toluene, 8.4 mmol) to generate $TaMe_3Cl_2$ *in situ*.[2] After stirring the mixture at room temperature for 1 hour, the solution is filtered to remove $ZnCl_2$. A suspension of [Ar-CMe_2-C_5H_4]Li (Ar = 3,5-dimethylphenyl, 1.0 g, 4.6 mmol) in 15 mL of toluene is added to the light greenish filtrate at 0 ºC. The mixture is stirred at 0 ºC for 1 hour and then at room temperature for another 3 hours. The yellow-orange suspension is filtered to remove the LiCl byproduct, and the solvent is removed from the filtrate *in vacuo*. To remove residual toluene, the solid product is stirred with 10 mL of pentane, which is subsequently pumped off. Extraction with pentane (3 × 50 mL), concentration of the extract and cooling to -78 ºC overnight gave 1.46 g of yellow-orange crystalline **1** (3.1 mmol, 67%). ^{1}H NMR (500 MHz, C_6D_6, 25 ºC) δ 6.79 (s, 2H, Ar *o*-H), 6.65 (s, 1H, Ar *p*-H), 5.59 (ps t, *J* = 2.6, Cp), 5.42 (ps t, *J* = 2.6, Cp), 2.12 (s, 6H, ArMe), 1.55 (s, 6H, CMe_2), 1.18 (s, 9H, TaMe). ^{13}C NMR (125.7 MHz, C_6D_6, 25 ºC) δ 149.0 (s, Cp *ipso*-C), 139.7 (s, Ar *ipso*-C), 137.7 (s, Ar *m*-C), 128.3 (d, *J* = 158, Ar *p*-CH), 124.0 (d, *J* = 155, Ar *o*-CH), 113.4 (d, *J* = 180, Cp CH), 107.3 (d, *J* = 177, Cp CH), 67.0 (q, *J* = 122, TaMe), 39.5 (s, *C*Me_2), 28.6 (q, *J* = 127, C*Me*$_2$), 21.6 (q, *J* = 126, ArMe). Anal. Calcd for $C_{19}H_{28}ClTa$: C, 48.3; H, 5.97. Found: C, 48.0; H, 5.85.

Synthesis of [η^1-$Me_2C_6H_2$-CMe_2-η^5-C_5H_4]Ta(^{n}Pr)(C_3H_6) (2). A stirred solution of **1** (394 mg, 0.833 mmol) in 30 mL of Et_2O is cooled to -50 ºC and ^{n}PrMgCl (0.88 mL of a 2.0 M solution in Et_2O, 1.75 mmol) is syringed in. The mixture is allowed to slowly warm to room temperature, during which the colour gradually changes to red. All volatiles are removed *in vacuo*, and the residue is extracted with pentane (2 × 30 mL). The pentane solution was concentrated and cooled to -78 ºC overnight, giving 110 mg of dark red crystals of **2**. Further concentration of the mother liquor and cooling to -78 ºC afforded another 19 mg of crystalline product (total 129 mg, 0.271 mmol, 33%). *Major isomer* (Me substituent on propene towards cyclopentadienyl): ^{1}H NMR (500 MHz, C_6D_6, 25 ºC) δ 6.76 (s, 2H, Ar H), 6.20 (m, 1H, Cp), 5.92 (m, 1H, Cp), 5.80 (m, 1H, Cp), 4.56 (m, 1H, Cp), 2.87 (dd, 1H, ^2J = 8.7, ^3J = 14.9, Ta(C*H*H'=CHMe)), 2.75 (m, 1H, Ta(CH_2=C*H*Me)), 2.48 (dd, 1H, ^2J = 8.7, ^3J = 10.5, Ta(CH*H*'=CHMe)), 2.42 (s, 3H, ArMe), 2.09 (s, 3H, ArMe), 1.85 (d, 3H, *J* = 7.3, TaCH_2=CH*Me*), 1.82 (m, 1H, TaCH_2C*H*H'Me), 1.55 (m, 1H, TaCH_2CH*H*'Me), 1.53 (m, 1H, TaC*H*H'CH_2Me), 1.50 (s, 3H, CMe_2), 1.18 (s, 3H, CMe_2), 1.03 (t, 3H, *J* = 7.0, TaCH_2CH_2*Me*), 0.39 (m, 1H, TaCH*H*'CH_2Me). ^{13}C NMR (125.7 MHz, C_6D_6, 25 ºC) δ 202.3 (s, Ar *o*-C), 165.8 (s, Cp *ipso*-C), 137.3, 136.7 and 136.3 (s, Ar

ipso- and *m*-C), 129.1 (d, overlapped, Ar CH), 123.1 (d, *J* = 152, Ar CH), 116.4 (d, *J* = 174, Cp CH), 104.0 (d, *J* = 175, Cp CH), 101.9 (d, *J* = 176, Cp CH), 96.6 (d, *J* = 173, Cp CH), 91.0 (t, *J* = 115, Ta*C*$H_2$$CH_2$Me), 88.8 (d, *J* = 145, Ta(CH_2=*C*HMe)), 84.2 (t, *J* = 145, Ta(*C*H_2=CHMe)), 42.0 (s, *C*Me_2), 32.7 (q, *J* = 127, C*Me*$_2$), 30.2 (q, *J* = 127, C*Me*$_2$), 25.3 (q, overlapped, ArMe), 24.7 (t, overlapped, TaCH_2*C*H_2Me), 21.7 (q, *J* = 126, ArMe), 21.3 (q, *J* = 127, Ta$CH_2$$CH_2$*Me*), 21.0 (q, *J* = 122, Ta(CH_2=CH*Me*). M*inor isomer* (Me substituent on propene away from cyclopentadienyl): ^{1}H NMR (500 MHz, C_6D_6, 25 ºC) δ 6.76 (s, 2H, Ar H), 6.12 (m, 1H, Cp), 5.95 (m, 1H, Cp), 5.78 (m, 1H, Cp), 4.68 (m, 1H, Cp), 3.79 (m, 1H, Ta(C*H*H'=CHMe), 2.53 (d, 3H, *J* = 6.3, Ta(CH_2=CH*Me*), 2.50 (s, 3H, ArMe), 2.08 (s, 3H ArMe), ~1.9 (m, 1H, TaCH_2C*H*H'Me), 1.78 (m, 1H, Ta(CH*H*'=CHMe), 1.74 (m, 1H, Ta(CH_2=C*H*Me)), ~1.6 (m, 1H, TaCH_2CH*H*'Me), 1.56 (m, 1H, TaC*H*H'CH_2Me), 1.50 (s, 3H, CMe_2), 1.27 (s, 3H, CMe_2), 1.00 (t, 3H, *J* = 7.3, Ta$CH_2$$CH_2$*Me*), 0.44 (m, 1H, TaCH*H*'CH_2Me). ^{13}C NMR (125.7 MHz, C_6D_6, 25 ºC) δ 204.3 (Ar *o*-C), 167.7 (Cp *ipso*-C), 138.7, 137.5 and 137.4 (Ar *ipso*- and *m*-C), 129.2 (Ar CH), 123.2 (Ar CH), 115.9 (Cp CH), 103.5 (Cp CH), 102.0 (Cp CH), 99.6 (Cp CH), 92.9 (d, *J* ≈ 140, Ta(CH_2=*C*HMe)), 90.7 (t, *J* ≈ 115, Ta(CH_2=*C*HMe)), 86.0 (t, *J* ≈ 145, Ta(*C*H_2=CHMe)), 42.2 (*C*Me_2), 32.7 (C*Me*$_2$), 29.6 (C*Me*$_2$), 26.1 (ArMe), 25.5 (TaCH_2*C*H_2Me), 23.0 (ArMe), 22.7 (Ta$CH_2$$CH_2$*Me*), 21.0 (Ta($CH_2$=CH*Me*). Anal. Calcd for $C_{22}H_{31}$Ta: C, 55.5; H, 6.56. Found: C, 56.3 ; H, 6.78.

Synthesis of {[η^6-Ar-CMe_2-η^5-C_5H_4]TaPr}$^+$[B(C_6F_5)$_4$]$^-$ (3). Solid [PhNMe_2H][B(C_6F_5)$_4$] (139 mg, 0.173 mmol) is added to a cold (-30 ºC) solution of **2** (83 mg, 0.174 mmol) in 3 mL of bromobenzene. The mixture is shaken and allowed to warm to room temperature, resulting in a clear brownish solution. Hexane is layered on top of the solution and after standing at -30 ºC overnight, dark brown needles are formed. Decanting the supernatant and washing with pentane gave 196 mg of **3** (0.154 mmol, 88%). Crystals suitable for X-ray analysis are obtained by diffusion of cyclohexane into a bromobenzene solution of **3** at room temperature. ^{1}H NMR (500 MHz, C_6D_5Br, -25 ºC) δ 4.55 (s, 1H, Ar *o*-H), 4.49 (s, 1H, Cp), 4.43 (s, 1H, Cp), 4.32, (s, 1H, Cp), 4.23 (s, 1H, Ar *o*-H), 4.17 (s, 1H, Cp), 2.22 (s, 1H, Ar *p*-H), 1.85 (s, 3H, ArMe), 1.73 (s, 3H, ArMe), 0.84 (ps t, *J* = 5.5, Ta$CH_2$$CH_2$*Me*), 0.61 (br m, 1H, TaC*H*H'CH_2Me), 0.58 (s, 3H, CMe_2), 0.40 (s, 3H, CMe_2), -0.54 (br m, 1H, TaCH*H*'CH_2Me), -1.9 (br, 1H, TaCH_2C*H*H'Me), -5.9 (br, 1H, TaCH_2CH*H*'Me). ^{13}C NMR* (125.7 MHz, C_6D_5Br, -30 ºC) δ 128.8 (s, Ar *m*-C), 127.7 (s, Ar *m*-C), 102.9 (d, *J* ≈ 180, Cp CH), 101.2 (d, *J* ≈ 180, Cp CH), 97.6 (d, *J* ≈ 175, Ar *o*-CH), 93.8 (d, *J* ≈ 170, Ar *p*-CH), 93.1 (d, *J* ≈ 175, Ar *o*-CH), 72.6 (d, *J* ≈ 185, Cp CH), 72.2 (s, Cp *ipso*-C), 71.7 (d, *J* ≈ 185, Cp CH), 60.4 (s, Ar *ipso*-C), 36.1 (s, *C*Me_2), 21.1,

20.7 (q, $J \approx 128$, ArMe), 20.3, 19.9 (q, $J \approx 128$, C*Me*$_2$), 16.3 (q, $J \approx 128$, TaCH$_2$CH$_2$*Me*), 11.4 (t, $J \approx 144$, Ta*C*H$_2$CH$_2$Me), -3.4 (TaCH$_2$*C*H$_2$Me). Anal. Calcd for $C_{49}H_{31}BBrF_{20}Ta$: C, 46.29; H, 2.46; Ta, 14.23. Found: C, 46.20; H, 2.42; Ta, 14.18.

*due to low solubility at -30 ºC, ^{13}C chemical shifts and CH-coupling constants are determined from a modified HSQC experiment with J_{CH} detection along the ^{13}C axis. Line broadening in the ^{1}H NMR spectrum due to the agostic interaction prevented detection of the corresponding ^{13}C frequency in the HSQC spectrum, but this resonance was found in the 1D ^{13}C{^{1}H} NMR spectrum.

Synthesis of {[η^6-Ar-CMe$_2$-η^5-C$_5$H$_4$]TaH}$^+$[B(C$_6$F$_5$)$_4$]$^-$ (4). An NMR tube containing a C_6D_5Br solution of **3** was degassed on a high-vacuum line and back-filled with 1 bar of H_2 at room temperature. The tube was shaken and analysed by NMR spectroscopy to be **4**. Attempts to isolate **4** by precipitation with hexane gave red oils that decomposed to dark brown unidentified species upon removal of the solvent. ^{1}H NMR (500 MHz, C_6D_5Br, -25 ºC) δ 5.42 (s, 1H, Cp), 5.05 (s, 1H, Ar *o*-H), 4.62 (s, 1H, Cp), 4.46 (s, 1H, Cp), 3.77 (s, 1H, Cp), 3.76 (s, 1H, Ar *p*-H), 3.55 (s, 1H, Ar *o*-H), 2.03 (s, 3H, ArMe), 1.76 (s, 3H, ArMe), 0.69 (s, 3H, CMe$_2$), 0.31 (s, 3H, CMe$_2$), -4.65 (s, 1H, TaH). ^{13}C NMR (125.7 MHz, C_6D_5Br, -25 ºC) δ 132.8 (s, Ar *m*-C), 129.4 (s, Ar *m*-C), 108.0 (d, J = 178, Cp CH), 102.3 (d, J = 173, Ar *o*-CH), 94.8 (d, J = 183, Cp CH), 90.5 (d, J = 174, Ar *p*-CH), 88.6 (d, J = 176, Ar *o*-CH), 73.9 (d, J = 182, Cp CH), 73.9 (s, Cp *ipso*-C), 71.0 (d, J = 184, Cp CH), 61.8 (s, Ar *ipso*-C), 35.4 (s, *C*Me$_2$), 22.6 (q, J = 130, ArMe), 21.1 (q, J = 130, ArMe), 20.4 (q, J = 128, C*Me*$_2$), 20.3 (q, J = 128, C*Me*$_2$).

NMR scale reaction of 4 with propene. A solution of **4** (ca. 5 mg) in C_6D_5Br was prepared as described above in an NMR tube. After removal of excess H_2, the tube was pressurized with 1 bar of propene at RT. A ^{1}H NMR spectrum taken ca. 10 min after mixing showed a mixture of **4** and **3** in approx. 1:1 ratio (no intermediates were observed). Within 1 hour, **3** was the only observable product by ^{1}H NMR.

Catalytic hydrogenation of 1-hexene using 4. An NMR tube (equipped with a Teflon Young valve), containing a solution of **3** (3.0 mg, 2.4 μmol) in 0.4 mL of C_6D_5Br and 20 equiv of 1-hexene, was attached to a high-vacuum line. The tube was frozen in liquid N_2 and degassed, after which H_2 was admitted. After closing the valve, the tube was brought to ambient temperature and the reaction was monitored by ^{1}H NMR. Gradual formation of n-hexane was observed (~70% conversion in 16h). The reaction goes to full conversion, and n-hexane was the only product observed.

Synthesis of {[η^6-Ar-CMe$_2$-η^5-C$_5$H$_4$]TaH(THF)}$^+$[B(C$_6$F$_5$)$_4$]$^-$ (4-THF). To a C_6D_5Br solution of **4** (prepared *in situ* as described above), a drop of THF-d_8 was added. NMR spectroscopy was consistent with formation of **4-THF**. On preparative scale, **3** (52.2 mg, 41.3 μmol) was dissolved in 1 mL of bromobenzene. The solution was degassed by three freeze-pump-thaw cycles and 1 bar of H_2 was admitted at room temperature. After stirring for 10 min, excess H_2 was removed and a few drops of THF were added. This solution was allowed to react at -30 ºC for 30 min, then hexane (ca. 3 mL) was added to precipitate the product. The solution was decanted and the solid washed with toluene and then pentane. Drying *in vacuo* afforded **4-THF** as a pink powder (32.7 mg, 69%). Recrystallization from bromobenzene/hexane gave analytically pure material. ^{1}H NMR (500 MHz, C_6D_5Br, 25 ºC) δ 5.97 (s, 1H, Cp), 4.95 (s, 1H, Ar *o*-H), 4.85 (s, 1H, Cp), 4.46 (s, 1H, Cp), 3.92 (s, 1H, Ar *p*-H), 3.37 (s, 1H, Cp), 3.08 (s, 1H, Ar *o*-H), 3.03 (br, 4H, THF), 2.10 (s, 3H, ArMe), 1.53 (s, 3H, ArMe), 1.27 (br m, 4H, THF), 0.78 (s, 3H, CMe_2), 0.28 (s, 3H, CMe_2), -3.98 (s, 1H, TaH). ^{13}C NMR (125.7 MHz, C_6D_5Br, 25 ºC) δ 133.4 (s, Ar *m*-C), 131.1 (s, Ar *m*-C), 106.1 (d, J = 175, Cp CH), 100.2 (d, J = 175, Ar *o*-CH), 98.7 (d, J = 185, Cp CH), 91.6 (d, J = 176, Ar *o*-CH), 89.4 (d, J = 174, Ar *p*-CH), 85.9 (br t, J = 155, THF), 77.7 (s, Cp *ipso*-C), 73.7 (d, J = 181, Cp CH), 71.5 (d, J = 183, Cp CH), 61.5 (s, Ar *ipso*-C), 34.6 (s, *C*Me$_2$), 27.2 (t, J = 135, THF), 22.5 (q, J = 129, ArMe), 21.2 (q, J = 128, C*Me*$_2$), 20.82 (q, J = 128, C*Me*$_2$), 20.80 (q, J = 128, ArMe). IR (nujol mull): 1760 (TaH). Anal. Calcd for $C_{44}H_{28}BF_{20}OTa$: C, 46.18; H, 2.47; Ta, 15.81. Found: C, 45.88; H, 2.58; Ta, 15.75.

Synthesis of {[η^6-Ar-CMe$_2$-η^5-C$_5$H$_4$]TaPr(CO)}$^+$[B(C$_6$F$_5$)$_4$]$^-$ (5). A solution of **3** (23.0 mg, 18.1 μmol) in 1 mL of C_6H_5Br is degassed, cooled to 0 ºC and subsequently pressurized with 1 bar of CO. After stirring at 0 ºC for 1 hour, excess CO is removed and the red solution is stirred with 1.5 mL of hexane. A red oil is precipitated, which solidifies in the course of a couple of hours. The supernatant is decanted and the residue is washed with pentane. Drying *in vacuo* gives **5** as a red powder in quantitative yield. ^{1}H NMR (500 MHz, C_6D_5Br, 20 ºC) δ 4.88 (s, 1H, Cp), 4.66 (s, 1H, Ar *o*-H), 4.63 (s, 1H, Cp), 4.37 (s, 1H, Cp), 4.26 (s, 1H, Ar *o*-H), 4.00 (s, 1H, Ar *p*-H), 3.73 (s, 1H, Cp), 2.00 (s, 3H, ArMe), 1.55 (s, 3H, ArMe), 1.00 (m, 1H, TaCH$_2$C*H*H'Me), 0.79 (ps t, 3H, J = 7.0, TaCH$_2$CH$_2$*Me*), 0.70 (s, 3H, CMe_2), 0.62 (m, 1H, TaCH$_2$CH*H'*Me), 0.57 (s, 3H, CMe_2), 0.02 (d ps t, 1H, $^2J \approx {}^3J$ = 13.0, $^3J'$ = 3.9, TaC*H*H'CH$_2$Me), -0.41 (ps t, 1H, $^2J \approx {}^3J$ = 13.0, $^3J'$ < 1, TaCH*H'*CH$_2$Me). ^{13}C NMR (125.7 MHz, C_6D_5Br, 20 ºC) δ 211.2 (s, CO), 136.0 (s, Ar *m*-C), 132.9 (s, Ar *m*-C), 111.2 (d, J = 184, Cp CH), 96.62 (d, $J \approx$ 175, Ar *o*-CH), 96.56 (d, $J \approx$ 175, Ar *o*-CH), 96.1 (d, J = 180, Cp CH), 92.6 (d, J = 177, Ar *p*-CH), 79.7

(d, *J* = 183, Cp CH), 75.1 (s, Cp *ipso*-C), 70.0 (d, *J* = 184, Cp CH), 66.8 (s, Ar *ipso*-C), 36.3 (s, *C*Me$_2$), 32.9 (t, *J* = 123, TaCH$_2$*C*H$_2$Me), 22.9 (q, *J* = 123, TaCH$_2$CH$_2$*Me*), 20.7 (q, *J* ≈ 130, ArMe), 20.1 (q, *J* ≈ 127, C*Me*$_2$), 20.0 (q, *J* ≈ 127, C*Me*$_2$), 19.8 (q, *J* ≈ 130, ArMe), 4.8 (t, *J* = 121, Ta*C*H$_2$CH$_2$Me). IR (film from C_6D_5Br): 2033 (CO). Anal. Calcd for $C_{44}H_{26}BF_{20}OTa$: C, 46.26; H, 2.28; Ta, 15.84. Found: C, 46.08 ; H, 2.32; Ta, 15.71.

Synthesis of {[Ar-CMe$_2$-η^5-C$_5$H$_4$]TaPr(SPh)$_2$}$^+$[B(C$_6$F$_5$)$_4$]$^-$ (6). To a solution of **3** (34 mg, 27 μmol) in 0.5 mL of C_6D_5Br at room temperature is added 7 mg of PhSSPh (ca. 1.2 eq). The mixture turns orange immediately and is analyzed by NMR to be **6** in ~95% purity. Addition of 2 mL of pentane results in precipitation of a dark orange oil, from which the supernatant is decanted. The oil is washed with pentane (2 × 2 mL) and then dried *in vacuo*, giving **6** as a light orange foamy solid (24 mg, 67%). ^{1}H NMR (500 MHz, C_6D_5Br, -25 ºC) δ 7.33-6.92 (m, 10H, SPh), 6.83 (s, 2H, Ar *o*-H), 6.73 (s, 1H, Ar *p*-H), 5.79 (s, 2H, Cp), 5.43 (s, 2H, Cp), 2.26 (s, 6H, ArMe), 1.93 (m, 2H, TaCH$_2$C*H*$_2$Me), 1.48 (s, 6H, CMe$_2$), 0.96 (t, *J* = 6.9, 2H, TaC*H*$_2$CH$_2$Me), 0.70 (t, *J* = 6.4, 3H, TaCH$_2$CH$_2$*Me*). ^{13}C NMR (125.7 MHz, C_6D_5Br, -25 ºC) δ 148.4 (s, Cp *ipso*-C), 144.1 (s, Ar *ipso*-C), 138.6 (s, Ar *m*-C), 137.0 (d, overlapped, SPh), 133.1 (d, *J* = 165, SPh), 130 (overlapped, Ar *p*-CH), 128.5 (s, SPh *ipso*-C), 127.1 (d, overlapped, SPh), 124.4 (d, *J* = 157, Ar *o*-CH), 112.6 (d, *J* = 183, Cp CH), 108.6 (d, *J* = 181, Cp CH), 86.1 (t, *J* = 124, Ta*C*H$_2$CH$_2$Me), 39.8 (s, *C*Me$_2$), 29.9 (q, *J* = 129, C*Me*$_2$), 29.1 (t, *J* = 123, TaCH$_2$*C*H$_2$Me), 21.8 (q, *J* = 126, ArMe), 20.0 (q, *J* = 127, TaCH$_2$CH$_2$*Me*). Anal. Calcd for $C_{55}H_{36}BF_{20}S_2Ta$: C, 49.57; H, 2.72; S, 4.81. Found: C, 48.56; H, 2.85; S, 4.63.

NMR data for the B(C$_6$F$_5$)$_4$ anion in 3-6. ^{13}C NMR (125.7 MHz, C_6D_5Br): δ 148.7 (d, J_{CF} = 242, *o*-CF), 138.6 (d, J_{CF} = 238, *p*-CF), 136.6 (d, J_{CF} = 241, *m*-CF), 124.7 (br, *ipso*-C). ^{19}F NMR (470.3 MHz, C_6D_5Br): δ -131.9 (br d, *o*-F), -161.7 (t, *J* = 21, *p*-F), -165.8 (br d, *m*-F).

References

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(2) Preparation and isolation of $TaMe_3Cl_2$: Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389. Use of commercially available toluene solutions of Me_2Zn in the synthesis renders isolation of volatile $TaMe_3Cl_2$ difficult. Preparation and use *in situ* proved to be a convenient alternative (monitoring the reaction of $TaCl_5$ with excess Me_2Zn (2.0 M in toluene) by ^1H NMR in C_6D_6 showed that $TaMe_3Cl_2$ is the only product, and no further alkylation occurs).

Part II: X-ray and DFT calculated structure of **4-THF**

Due to the weak scattering power of the crystal used, the location of the hydride ligand in the X-ray crystal structure determination was ambiguous. In the difference Fourier map a reasonable position for the hydride was found (Ta-H 1.79 Å). This position was not stable in the refinement, but in good agreement with the DFT calculated structure (vide infra). Therefore, in the refinement of the X-ray crystal structure of **4-THF** restrain instructions (*DFIX*, *DANG*) for the hydride were applied, resulting in a Ta-H distance of 1.762(16) Å.

Geometry optimization of **4-THF** was performed using the DFT/B3LYP method implemented in Gaussian 03[1] without symmetry constraints. The structure obtained by X-ray diffraction was used as starting point, and the hydride ligand (which could not be unambiguously located in the X-ray structure determination) was placed 2.02 Å away from the Ta center (H-Ta-O(THF) angle 100.8 º). The basis sets LANL2DZ and 6-311G(d) were employed on Ta and C/H/O, respectively. The structure converged to a Ta-H distance of 1.77 Å. All other metrical parameters are in good agreement with the experimental structure. Frequency analysis confirmed this structure to be a minimum with a calculated Ta-H stretching frequency of 1819 cm^{-1} (IR: 1760 cm^{-1}).

Atomic coordinates of optimized structure:

C 1.9210678205 0.6941734817 -2.4006763386
O 1.9065016953 0.5090178166 -0.9415085693
C 3.2839631819 0.5933159276 -0.4143262319
C 4.1011879066 1.1768650834 -1.5559071656
C 3.3889656126 0.622986386 -2.7979570135
Ta 0.176022711 -0.2060914719 0.2676566703
C -1.6817602173 1.2794213941 -0.4739266345
C -2.0384149898 0.2426020603 0.4726574261
C -1.5677613934 0.3654468567 1.8370972356
C -0.5455634337 1.2550492864 2.155681743
C 0.033184804 2.0058573761 1.08174577
C -0.6646151214 2.1715355593 -0.1680983406
C -0.0494686298 1.4277145603 3.5609295566
C -2.7175727564 -1.0726084973 0.0202341552

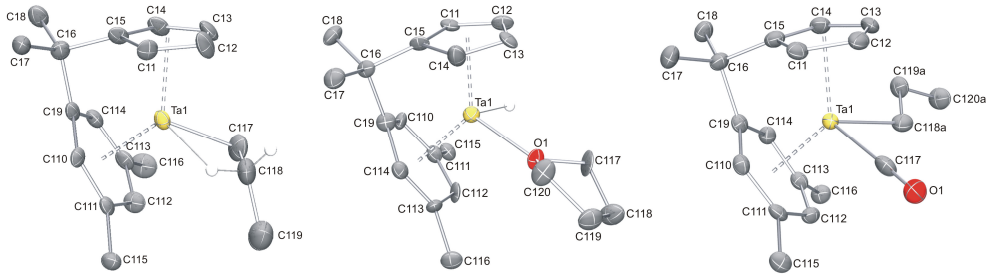
C -1.4055279994 -1.8455890677 -0.1749926511
C -0.5808877051 -2.3251492872 0.9055636589
C 0.7238310069 -2.5879683435 0.3838348772
C 0.7212840439 -2.2638619324 -0.9832728739
C -0.5672059666 -1.7786177438 -1.3476225403
C -0.2831525046 3.2967465406 -1.0869567335
C -3.5215550457 -0.9345794432 -1.2780983756
C -3.6284732431 -1.7030366119 1.0817921241
H 1.5707284041 -2.3472383092 -1.6465122802
H -2.1962621022 1.3639842287 -1.4222209237
H -4.3770108036 -0.2717703927 -1.1270863637
H -3.9055444874 -1.9104709593 -1.5815767778
H -4.477598995 -1.0481081305 1.2913200096
H -0.6417848679 3.1404333331 -2.1052274689
H 3.2459376764 1.2028114119 0.4848185846
H 3.5918008004 -0.4185134513 -0.1461194452
H -0.2712420186 0.5584892901 4.1802759891
H 1.2964792419 -0.0819635852 -2.837968534
H 1.4792270979 1.6689300423 -2.6102190838
H 1.0267581892 1.6031501264 3.5830403793
H -0.8984214687 -2.5543262722 1.9100381831
H 0.876904838 2.6495429708 1.2972861676
H -2.9416145874 -0.5435888299 -2.1151751265
H 0.7983968029 3.4471605078 -1.1096626314
H -0.8857358288 -1.5279081749 -2.3475059367
H -0.7227028167 4.2292210638 -0.7183250113
H 4.0632162719 2.2694498161 -1.5427437676
H -0.5373242076 2.2985235645 4.0110750386
H 1.5550109646 -2.9851196543 0.9456969172
H 5.1485666494 0.8779328513 -1.4977490893
H -3.1258301245 -1.9087617588 2.0267470248
H 3.6902162014 -0.4111305188 -2.985517171
H -4.0187025893 -2.6550143613 0.7157264574
H -1.9880921472 -0.2461210464 2.6232859276
H 3.5932812528 1.199149254 -3.7013340503
H 1.4205189657 -0.3480296107 1.5125547183

[1] **Gaussian 03**, *Revision B.05*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian Inc.*, Pittsburgh PA, 2003.

Part III: Description of disorder in the X-ray structure of **5**

Crystals suitable for X-ray diffraction were obtained by slow diffusion of cyclohexane into a bromobenzene solution of **5** at room temperature. Refinement was frustrated by substitutional disorder: part of the propyl ligand was substituted for Br. A substitutional disorder model resulted in a reasonable refinement, in which the s.o.f of Br refined to a value of 0.089(2). Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2)$ = 0.0820 for 8828 reflections and $R(F)$ = 0.0334 for 7297 reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 619 parameters.

Table S1: Ta-C and C-C bond lengths of the coordinated C_6-fragment



	3	4-THF	5
Ta(1)-C(19)$_{ipso}$	2.300(6)	2.247(8)	2.284(4)
Ta(1)-C(110)$_{ortho}$	2.361(6)	2.398(7)	2.413(3)
Ta(1)-C(114)$_{ortho'}$	2.391(6)	2.407(7)	2.399(4)
Ta(1)-C(111)$_{meta}$	2.474(6)	2.459(8)	2.476(3)
Ta(1)-C(113)$_{meta'}$	2.425(7)	2.481(8)	2.511(3)
Ta(1)-C(112)$_{para}$	2.352(8)	2.332(7)	2.399(4)
C(19)–C(110)	1.450(10)	1.463(11)	1.428(5)
C(110)–C(111)	1.390(10)	1.384(11)	1.388(5)
C(111)–C(112)	1.426(9)	1.426(11)	1.422(4)
C(112)–C(113)	1.447(11)	1.428(11)	1.417(5)
C(113)–C(114)	1.378(10)	1.365(11)	1.399(5)
C(114)–C(19)	1.431(9)	1.433(11)	1.440(4)
ring puckering	8.6(5)	14.8(5)	11.4(4)